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(54) Title: ELECTRICALLY CONDUCTING POLYMERS AND THEIR MANUFACTURE (57) Abstract A conductive polymer comprises chains composed of resonant (aromatic and/or heterocyclic) rings in which conjugation extends from end to end of the molecule and cross-links between these chains which consist of aromatic groups conjugated to the chains that they link. In this way the polymer conducts from molecule to molecule and in principle may be isotropically conductive. Preferably, the polymer chains are selected from polyaniline, polypyrrole, polythiophene, poly- <i>p</i> -phenylene, poly-(<i>p</i> -phenylene sulfide) and poly- <i>N</i> -vinylcarbazole. The resonant groups may comprise carbocyclic or heterocyclic aromatic groups or π -bonded aliphatic groups; <i>p</i> -phenylene groups and <i>p</i> -phenylene-vinylene groups are preferred. Such polymers can be made by a conjugative condensation reaction catalysed by a palladium compound. Three such condensation reactions are established and are named according to their respective authors as the <i>Suzuki</i> , <i>Stille</i> , and <i>Heck</i> reactions; the <i>Suzuki</i> reaction is preferred.		

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Electrically Conducting Polymers and their Manufacture

This invention relates to polymers that are inherently electrically conductive and to a method of making them. One of the applications for which the polymers may be used is in the control of electric fields in cable joints.

A variety of electrically conducting polymers have been discovered and a number of them are now finding useful applications. Among them are polyaniline, polypyrrole, polyacetylene, polythiophene, poly-*p*-phenylene, poly-*(p*-phenylene sulfide) and poly-*N*-vinylcarbazole.

All of these established conducting polymers have an essentially one-dimensional structure composed of resonant (aromatic and/or heterocyclic) rings connected to form a single chain in which conjugation extends from end to end of the molecule. A consequence of this is that they conduct primarily along the length of the molecule and have relatively small conductivities unless the molecules are aligned by orientation, and then conduct well in only one direction.

It is an object of the present invention to provide novel conductive polymers which have enhanced conductance in directions other than along the polymer chains and are potentially isotropically conductive.

The polymers in accordance with the invention comprise chains composed of resonant (aromatic and/or heterocyclic) rings in which conjugation extends from end to end of the molecule and crosslinks between these chains and is characterised in that such crosslinks consist of resonant groups conjugated to the chains that they link.

Preferably the polymer chains are selected from polyaniline, polypyrrole, polythiophene, poly-*p*-phenylene,

poly-(*p*-phenylene sulfide) and poly-*N*-vinylcarbazole.

The resonant groups constituting the crosslinks may be carbocyclic or heterocyclic aromatic groups, conjugated π -bonded aliphatic groups, or combinations of any of these.

5 We prefer that (apart from any parts contributed by sidechains already present in the polymer chains) they are selected from *p*-phenylene groups, *p*-phenylene-vinylene groups and sequences of one or both of these.

In accordance with the other main aspect of the
10 invention, a process for making such polymers comprises a conjugative condensation reaction catalysed by a palladium compound.

Three such condensation reactions are established and are named according to their respective authors as the
15 *Suzuki*, *Stille*, and *Heck* reactions. Our current preference is for the *Suzuki* reaction.

The *Suzuki* reaction requires the prior introduction into one of the aromatic molecules to be linked of a leaving group selected from halides (preferably bromine) and the triflate
20 group (also called trifluoromethane sulfonate). Preferably these groups are introduced into the polymer chains. The other molecule to be linked (preferably the relatively small molecule that is to provide the crosslinking groups) is pre-reacted with an organoboron compound to introduce -B(OH)₂
25 substituents. Practical catalysts for the condensation reaction between these groups to form notionally single bonds that bridge the resonant systems of the two molecules are dichlorobis[1,1'-bis(diphenyl phosphino)ferrocene]-palladium(II), which we prefer on grounds of stability and
30 ease of handling, and tetrakis(triphenylphosphine) palladium(0). Other catalysts of the same class may be used

if available, but are not known to have any advantage. The Suzuki reaction requires aqueous base to be present, and we prefer the conventional use of potassium phosphate (triposassium orthophosphate).

5 The Stille reaction is closely similar and may use the same catalysts. The only fundamental distinction is that the Stille reaction introduces $-\text{SnR}_3$ groups, instead of $-\text{B}(\text{OH})_2$ groups, into the second molecule to be linked.

 The Heck reaction is a little different in that it
10 requires a pendant alkene group in one of the molecules to be linked. This is reacted with an arylpalladium group introduced into the other molecule to be linked, and since this group is labile it is invariably generated *in situ*. Four reactions may be used for this purpose:

- 15 reaction of a bromo- substituent with a palladium-triarylphosphine complex;
- reaction of an iodo- substituent with palladium acetate in the presence of a base;
- reaction of a substituent group selected from $-\text{HgR}$ and
20 $-\text{HgX}$ (where R is an aromatic group and X is halide or triflate) with lithium palladium trichloride; and
- direct reaction of the unsubstituted aromatic molecule with palladium acetate (or metallic palladium and silver acetate) in acetic acid.

25 The Heck reaction, rather than the others, is appropriate to forming *p*-phenylene-vinylene crosslinks.

 If the crosslinking reaction is carried out in dilute solution, the product will normally be obtained as a powder which, because it is crosslinked, will be infusible,
30 insoluble and generally difficult to use, except as a conductive filler in polymers and coating compositions.

Preferably, therefore, the crosslinking reaction is carried out in a concentrated solution from which solvent may evaporate during and/or after the reaction to deposit the crosslinked product as a continuous coating.

5 At least some of the polymers in accordance with the invention have been found to have markedly non-linear electrical properties, with conductivities at even 10 -20V in some cases two or three orders of magnitude higher than in the ohmic region at low voltages; thus polymers whose
10 conductivity as measured in the ohmic region appears quite inadequate may be usefully conductive at voltages in the kV range.

 In the jointing of high-voltage electric power cables with polymeric dielectric, electrostatic fields need to be
15 precisely controlled to avoid local stress concentrations sufficient to risk electrical breakdown and degradation at transient peaks and eventual gross failure, and this requires careful attention to the place where the dielectric screen of the cable is terminated. One current practice is to chamfer
20 the edge of the screen, but this entails the loss of at least about 0.5mm of the radial thickness of the dielectric where the screen has been removed from it, and this is increasingly unacceptable as cables are designed to operate at higher stress levels. Alternatively the screen is terminated in a
25 plane normal to the cable axis, and as it is impracticable to make a cut with complete accuracy and total repeatability (and in most cases impossible to re-cut if anything goes wrong) this is achieved by removing the screen a little further than desired and restoring to the required position
30 by applying a conductive coating based on carbon black. This coating is not of great strength and is at risk of damage

when other cable components (especially the "stress cone") are slid into place. In the nature of the problem, the coating is inaccessible and cannot be inspected for such damage after the stress cone is in place, since removing it would multiply the risk. It is suspected that such damage may be responsible for a significant fraction of joint failures in service. By forming *in situ* in a coating on the joint the polymers of the present invention, a tougher conductive coating can be formed and the risk substantially reduced.

The invention will be further described, by way of example, with reference to the accompanying drawings in which each of equations 1-4 represents a step in the synthesis of one of the conducting polymers to be described and each of Figures 1-3 is a graph showing a current/voltage characteristic of one polymer in accordance with the invention.

Example 1

A copolymer of (α -thiophenediyl) benzyliidene and its *p*-bromo derivative was synthesised from commercially available starting materials as follows (Equation 1). Thiophene (25.2 g), benzaldehyde (15.0 g) and *p*-bromobenzaldehyde (26.3 g) were dissolved in dichloromethane (120 ml) in a 3-necked flask under a nitrogen atmosphere. This solution was stirred and cooled to 0°C. Boron trifluoride etherate (14.3 g) was then added dropwise and the mixture refluxed for 17 hours. After this time the solvent was removed leaving a viscous dark brown liquid. This liquid was dissolved in dichloromethane (400 ml), precipitated into methanol, washed with methanol and dried. The product, a copolymer of (α -thiophenediyl)benzyliidene and (α -thiophenediyl)

p-bromobenzylidene, was a red/brown solid.

The above procedure and quantities give a polymer with about 30% of the phenyl rings brominated; the degree of bromination could be altered by varying the ratio of benzaldehyde to *p*-bromobenzaldehyde.

The copolymer of (α -thiophenediyl) benzylidene and (α -thiophenediyl) *p*-bromobenzylidene made as described (2.0 g) was dissolved in the volume of tetrahydrofuran indicated in Table 1 and 9 ml of 2M aqueous potassium phosphate added to form a first solution ("Solution A").

Dichlorobis[1,1'-bis(diphenylphosphino)ferrocene] palladium(II) (0.02 g) as catalyst and 4,4'-biphenyl diboronic acid (in amount tabulated, calculated to produce the degree of crosslinking indicated on the basis of total reaction) to form a crosslinking group were dissolved in tetrahydrofuran (6 ml) to form a second solution ("Solution B").

The final cross-linked polymer was produced by thoroughly mixing the whole of Solutions A and B and heating under reflux conditions for 24 hours. The product was obtained as a black insoluble powder, washed and dried; portions were pressed into circular plaques 20.1 mm² in area and about 0.5 to 1 mm thick under a pressure of 25 tonnes; the plaques were sandwiched between electrodes and current/voltage relationships plotted using a Keithley 617 Electrometer, each reading being taken after stabilising for 5 minutes. For initial comparison, the ohms law region of each plaque was determined (for accuracy by determining the part of the characteristic in which the gradient of log V vs log I was 1) and the resistivity calculated and tabulated for that region. This procedure will be more fully described

below, with reference to Figures 1-3.

Table 1

Run no	Solvent volume (ml)	Amount of diboronic acid (g)	nominal % crosslinking	conductivity (ohm cm) ⁻¹
1	40	0.75	30	3×10^{-9}
2	40	0.50	20	1×10^{-15}
3	40	0.25	10	8×10^{-12}
4	40	0.25	10	5×10^{-7}
5	20	0.25	10	2×10^{-8}
6	10	0.25	10	1×10^{-8}

Example 2

5 This was substantially the same as Example 1 Run 1 except that the volume of solvent in each of solutions A and B was reduced until the solution became very viscous and the final polymer was obtained by mixing the solutions and applying the mixture immediately to a dry surface of an inert polymer
10 material and then heating to 50°C for 24 hours to cure the coating and remove the residual solvent from it. The final cross-linked polymer was a black insoluble solid.

Example 3

This was similar to Example 1 except that it was based on a
15 homopolymer of *p*-bromobenzaldehyde instead of the copolymer; in the first stage of synthesis, the benzaldehyde was (of course) omitted and the amount of *p*-bromobenzaldehyde doubled to 52.6 g; subsequent procedure was as before and the results were as follows:

Table 2

Run no	Solvent volume (ml)	Amount of diboronic acid (g)	nominal % crosslinking	conductivity (ohm cm) ⁻¹
7	40	0.75	30	8×10^{-10}
8	40	0.50	20	1×10^{-15}
9	40	0.25	10	5×10^{-8}
10	40	0.25	10	4×10^{-8}
11	20	0.25	10	3×10^{-8}
12	10	0.25	10	1×10^{-8}

To clarify the procedure for estimating conductivities and by way of illustration, Figures 1-3 show data for Run 10 of this Example, respectively in log/log, linear/linear and enlarged log/log format. Figures 1 and 2 clearly demonstrate the highly non-linear characteristics of this polymer for voltages of each polarity, while Figure 3 shows how a log-log plot (here restricted to the relevant part of the "positive" polarity side of the graph) more clearly identifies the Ohm's law region in which the gradient of Figure 2 is constant and that of figures 1 and 3 is unity. Having identified the linear region of Figure 2 in this way, its gradient and thus the resistance of the plaque can be determined and conductivity (and/or resistivity) calculated in the usual way.

Example 4

Poly(3-phenyl-2,5-thiophene) was synthesised in three stages via 3-phenyl-2-chlorothiophene as follows (Equations 2-4).
2,5-Dichlorothiophene (5.0 g), dichloromethane (20 ml) and

benzene (8.8 ml) were mixed together in a 2-necked round bottomed flask, cooled to 0°C and stirred for 10 minutes. Aluminium chloride (4.4 g) was then added slowly over a period of 5 minutes. The mixture was stirred at 0°C for 30 minutes, then at room temperature for 1 hour and then refluxed for 30 minutes. After this time the mixture was poured into ice-water (120 ml) and the product, 3-phenyl-2-chlorothiophene, extracted with dichloromethane (200 ml) and further purified by column chromatography. 3-Phenyl-2-chlorothiophene (2.0 g) was dissolved in carbon tetrachloride (20 ml) and sulfuryl chloride (2.08 g) added. The mixture was refluxed for 60 hours then poured into ice-water (150 ml). The product was extracted with carbon tetrachloride (200 ml) and purified by column chromatography. The product, 3-phenyl-2,5-dichlorothiophene, was a colourless oil.

A sample of the 3-phenyl-2,5-dichlorothiophene so produced was polymerised as follows: nickel chloride (0.155 g), dipyridyl (0.187 g), triphenyl phosphine (6.27 g), zinc (4.84 g) and the monomer, 3-phenyl-2,5-dichlorothiophene (3.91 g), were added to dry *N,N*-dimethylacetamide (8 ml) under a nitrogen atmosphere. The mixture was stirred at 90°C for 3 hours then cooled and diluted with *N*-methyl pyrrolidone (30 ml). The reaction mixture was filtered and precipitated into 10% hydrochloric acid in methanol (1.5 l). The product was filtered, washed with methanol and dried giving the product, poly(3-phenyl-2,5-thiophene), as a red/brown powder.

A sample of this poly(3-phenyl-2,5-thiophene) (4.0 g) was dissolved in carbon tetrachloride (90 ml) in a 2-necked round bottomed flask. The flask was covered with aluminium

foil to eliminate light from the reaction. Thallic acetate (0.124g) was added and the mixture stirred for a few minutes. Bromine (1.30 ml) was added dropwise and the reaction mixture refluxed for 3 hours. After this time the flask was cooled
5 and the solution precipitated into methanol. The solid polymer was filtered, washed with methanol and dried. The product, poly(3-(*p*-bromophenyl)-2,5-thiophene), was a yellow solid.

The above procedure and quantities give a polymer with
10 substantially all of the phenyl rings mono-brominated. The degree of bromination could be reduced by using smaller amounts of bromine and varying the reaction time.

Brominated poly(3-phenyl-2,5-thiophene) (2.42 g) made as just described was dissolved in tetrahydrofuran (20 ml) and
15 9 ml of 2M aqueous potassium phosphate added together with 0.02g of dichlorobis [1,1'-bis(diphenyl phosphino) ferrocene] palladium (II) and the tabulated amounts of 4,4'-biphenyl diboronic acid. The mixture was refluxed for 24 hours and the product (a brown solid) recovered and tested as in Example 1;
20 results are given in Table 3 below, together with those for Examples 4 and 5.

Example 4

This was substantially the same as Run 15 (or Run 16) of Example 3 except that instead of the reaction mixture being
25 refluxed for 24 hours it was simply allowed to react at ambient temperature for the same length of time; it is suspected that the crosslinking reaction may not have been complete when the product was recovered.

Example 5

30 This was also similar to Run 15 (or Run 16) of Example 3, except that in the polymeration reaction 10 mole % of the

3-phenyl-2,5-dichlorothiophene was replaced by 2,5-dichlorothiophene.

Table 3

Run or Example no.	Amount of diboronic acid (g)	Nominal degree of crosslinking (%)	conductivity (ohm.cm) ⁻¹
Run 13	0.125	5	2×10^{-10}
Run 14			7×10^{-10}
Run 15	0.25	10	4×10^{-10}
Run 16			3×10^{-11}
Run 17	0.375	15	3×10^{-15}
Run 18	0.75	30	3×10^{-10}
Example 4	0.25	10	4×10^{-12}
Example 5	0.25	10	1×10^{-9}

5 Example 6

This was similar to Run 18, except that in similar manner to Example 2 the reagents were prepared in two separate solutions and then the volume of solvent was in each reduced until the solution became very viscous. The final cross-linked polymer was produced by thoroughly mixing the two solutions, applying the mixture to a dry surface of inert polymer and heating to 50°C for 24 hours to cure the coated polymer mixture and remove the residual solvent. The final cross-linked polymer was a brown insoluble solid.

15 Examples 7-8

Tetrakis(triphenylphosphine)palladium(0) (0.02 g) as catalyst and 4,4'-biphenyl diboronic acid (0.334 g) to form crosslinking groups were dissolved in tetrahydrofuran (10 ml)

and the volume of the solvent reduced until the solution became very viscous and Examples 2 and 6 respectively were repeated except that this solution was used instead of the solution containing dichlorobis[1,1'-bis(diphenylphosphino)ferrocene] palladium(II); results were similar.

Example 9

A 250kV power cable insulated with cross-linked polyethylene was prepared for jointing in the usual way and the dielectric screen trimmed normal to the cable axis some 5 mm beyond the design position of the screen end. At the latter position, an accurate square edge was defined by temporary application of a masking tape. The mixed solution from Example 2 was painted on the bare area of dielectric between the masking tape and the cut edge of the screen and for a few millimetres onto the screen. The coated area was heated to a temperature of about 50°C by a portable gas heater for 24 hours while work continued on other parts of the joint (the completion of a complete cable joint at such supertension voltages takes several days, and the reaction time is not unacceptable).

CLAIMS

- 1 A conductive polymer comprising chains composed of resonant rings in which conjugation extends from end to end of the molecule and crosslinks between these chains
- 5 *characterised in that* such crosslinks consist of aromatic groups conjugated to the chains that they link.
- 2 A conductive polymer as claimed in claim 1 in which the chains are polyaniline.
- 3 A conductive polymer as claimed in claim 1 in which the
- 10 chains are polypyrrole.
- 4 A conductive polymer as claimed in claim 1 in which the chains are polythiophene.
- 5 A conductive polymer as claimed in claim 1 in which the chains are poly-*p*-phenylene.
- 15 6 A conductive polymer as claimed in claim 1 in which the chains are poly-(*p*-phenylene sulfide).
- 7 A conductive polymer as claimed in claim 1 in which the chains are poly-*N*-vinylcarbazole.
- 8 A conductive polymer as claimed in any one of claims 1-7
- 20 in which the resonant groups constituting the crosslinks comprise carbocyclic aromatic groups.
- 9 A conductive polymer as claimed in any one of claims 1-8 in which the resonant groups constituting the crosslinks comprise heterocyclic aromatic groups.
- 25 10 A conductive polymer as claimed in any one of claims 1-9 in which the resonant groups constituting the crosslinks comprise conjugated π -bonded aliphatic groups.
- 11 A conductive polymer as claimed in any one of claims 1-7 in which the resonant groups constituting the crosslinks
- 30 consist (apart from any parts contributed by sidechains already present in the polymer chains) of *p*-phenylene groups.

12 A conductive polymer as claimed in any one of claims 1-7
in which the resonant groups constituting the crosslinks
consist (apart from any parts contributed by sidechains
already present in the polymer chains) of *p*-phenylene-
5 vinylene groups.

13 A conductive polymer substantially as described with
reference to any one of Examples 1 and 3-5.

14 A conductive polymer substantially as described with
reference to any one of Examples 2 and 6-8.

10 15 A process for making a polymer comprising chains
composed of resonant rings in which conjugation extends from
end to end of the molecule and crosslinks between these
chains consisting of aromatic groups conjugated to the
chains that they link, the process comprising a conjugative
15 condensation reaction catalysed by a palladium compound.

16 A process as claimed in claim 15 in which the resonant
groups constituting the crosslinks comprise carbocyclic
aromatic groups.

17 A process as claimed in claim 15 or claim 16 in which
20 the resonant groups constituting the crosslinks comprise
heterocyclic aromatic groups.

18 A process as claimed in any one of claims 15-17 in which
the resonant groups constituting the crosslinks comprise
conjugated π -bonded aliphatic groups.

25 19 A process as claimed in any one of claims 15-18 in which
the condensation reaction is a Suzuki reaction.

20 A process as claimed in any one of claims 15-18 in which
the condensation reaction is a *Stille* reaction.

21 A process as claimed in any one of claims 15-20 in which
30 the resonant groups constituting the side-chains are
polyphenylene groups.

- 22 A process as claimed in any one of claims 15-18 in which the condensation reaction is a *Heck* reaction.
- 23 A process as claimed in claim 22 in which the *Heck* reaction includes the reaction of a bromo- substituent with a
5 palladium-triarylphosphine complex.
- 24 A process as claimed in claim 22 in which the *Heck* reaction includes the reaction of an iodo- substituent with palladium acetate in the presence of a base.
- 25 A process as claimed in claim 22 in which the *Heck*
10 reaction includes the reaction of a substituent group selected from -HgR and -HgX (where R is an aromatic group and X is halide or triflate) with lithium palladium trichloride.
- 26 A process as claimed in claim 22 in which the *Heck* reaction includes the direct reaction of the unsubstituted
15 aromatic molecule with palladium acetate (or metallic palladium and silver acetate) in acetic acid.
- 27 A process as claimed in any one of claims 15-26 in which the crosslinking reaction is carried out in a concentrated solution from which solvent may evaporate during and/or after
20 the reaction to deposit the crosslinked product as a continuous coating.
- 28 A process for making a conductive polymer substantially as described with reference to any one of Examples 1 and 2-5.
- 29 A process for making a conductive polymer substantially
25 as described with reference to any one of Examples 2 and 6-8.
- 30 A high-voltage electric cable joint comprising a screen incorporating a conductive polymer as claimed in any one of claims 1-13.
- 31 A high-voltage electric cable joint comprising a screen
30 incorporating a conductive polymer made by a process claimed in any one of claims 15-28.

32 A high-voltage electric cable joint substantially as described with reference to Example 9.

33 A method of making a high-voltage cable joint substantially as described with reference to Example 9.

AMENDED CLAIMS

[received by the International Bureau on 28 April 1997 (28.04.97);
original claims 1-33 replaced by amended claims 1-27 (3 pages)]

- 1 A process for making a polymer comprising chains
composed of resonant rings in which conjugation extends from
end to end of the molecule and crosslinks between these
5 chains consisting of aromatic groups conjugated to the
chains that they link, the process comprising a conjugative
condensation reaction catalysed by a palladium compound.
- 2 A process as claimed in claim 1 in which the resonant
groups constituting the crosslinks comprise carbocyclic
10 aromatic groups.
- 3 A process as claimed in claim 1 or claim 2 in which the
resonant groups constituting the crosslinks comprise
heterocyclic aromatic groups.
- 4 A process as claimed in any one of claims 1-3 in which
15 the resonant groups constituting the crosslinks comprise
conjugated π -bonded aliphatic groups.
- 5 A process as claimed in any one of claims 1-4 in which
the condensation reaction is a *Suzuki* reaction.
- 6 A process as claimed in any one of claims 1-4 in which
20 the condensation reaction is a *Stille* reaction.
- 7 A process as claimed in any one of claims 1-6 in which
the resonant groups constituting the side-chains are
polyphenylene groups.
- 8 A process as claimed in any one of claims 1-4 in which
25 the condensation reaction is a *Heck* reaction.
- 9 A process as claimed in claim 8 in which the *Heck*
reaction includes the reaction of a bromo- substituent with a
palladium-triarylphosphine complex.
- 10 A process as claimed in claim 8 in which the *Heck*
30 reaction includes the reaction of an iodo- substituent with
palladium acetate in the presence of a base.

AMENDED SHEET (ARTICLE 19)

- 11 A process as claimed in claim 8 in which the *Heck* reaction includes the reaction of a substituent group selected from -HgR and -HgX (where R is an aromatic group and X is halide or triflate) with lithium palladium trichloride.
- 5 12 A process as claimed in claim 8 in which the *Heck* reaction includes the direct reaction of the unsubstituted aromatic molecule with palladium acetate (or metallic palladium and silver acetate) in acetic acid.
- 13 A process as claimed in any one of claims 1-12 in which
10 the crosslinking reaction is carried out in a concentrated solution from which solvent may evaporate during and/or after the reaction to deposit the crosslinked product as a continuous coating.
- 14 A high-voltage electric cable joint comprising a screen
15 incorporating a conductive polymer made by a process claimed in any one of claims 1-13.
- 15 A conductive polymer comprising chains composed of resonant rings in which conjugation extends from end to end of the molecule and crosslinks between these chains
20 characterised in that such crosslinks consist of aromatic groups conjugated to the chains that they link by a process comprising a conjugative condensation reaction catalysed by a palladium compound.
- 16 A conductive polymer as claimed in claim 15 in which the
25 chains are polyaniline.
- 17 A conductive polymer as claimed in claim 15 in which the chains are polypyrrole.
- 18 A conductive polymer as claimed in claim 15 in which the chains are polythiophene.
- 30 19 A conductive polymer as claimed in claim 15 in which the chains are poly-*p*-phenylene.

AMENDED SHEET (ARTICLE 19)

20 A conductive polymer as claimed in claim 15 in which the chains are poly-(p-phenylene sulfide).

21 A conductive polymer as claimed in claim 15 in which the chains are poly-N-vinylcarbazole.

5 22 A conductive polymer as claimed in any one of claims 15-21 in which the resonant groups constituting the crosslinks comprise carbocyclic aromatic groups.

23 A conductive polymer as claimed in any one of claims 15-22 in which the resonant groups constituting the
10 crosslinks comprise heterocyclic aromatic groups.

24 A conductive polymer as claimed in any one of claims 15-23 in which the resonant groups constituting the crosslinks comprise conjugated π -bonded aliphatic groups.

25 A conductive polymer as claimed in claim 15 in which the
15 resonant groups constituting the crosslinks consist (apart from any parts contributed by sidechains already present in the polymer chains) of p-phenylene groups.

26 A conductive polymer as claimed in claim 15 in which the resonant groups constituting the crosslinks consist (apart
20 from any parts contributed by sidechains already present in the polymer chains) of p-phenylene-vinylene groups.

27 A high-voltage electric cable joint comprising a screen incorporating a conductive polymer as claimed in any one of claims 15-26.

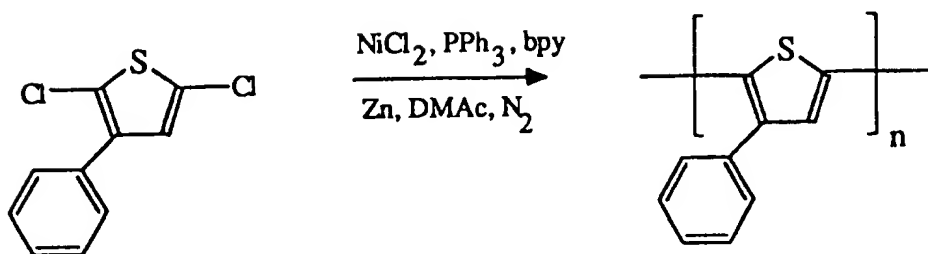
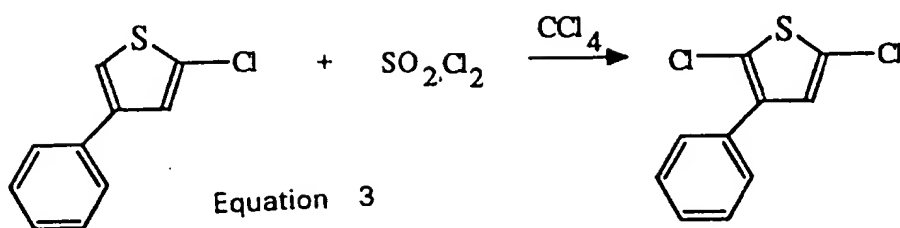
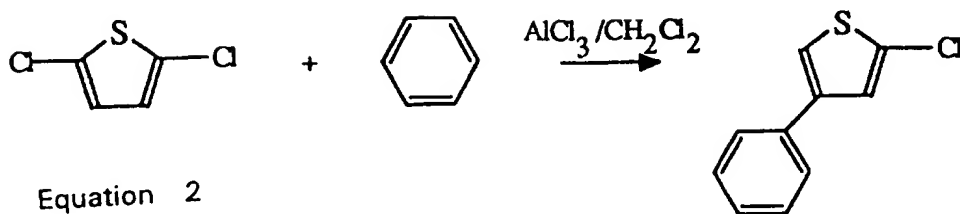
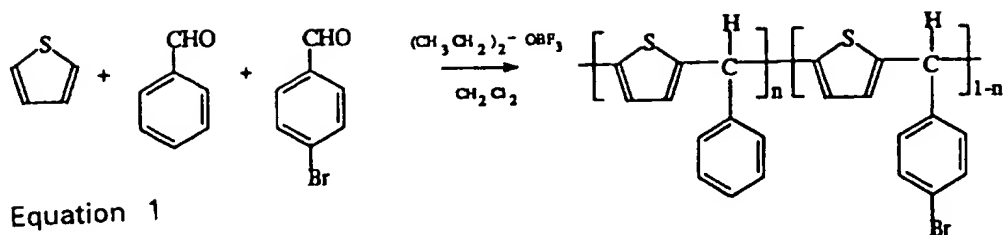
AMENDED SHEET (ARTICLE 19)

Statement under Article 19 PCT

In the opinion of the applicants, cited US5254627 is of
5 more than background interest, and the claims have been
amended to distinguish the invention clearly from what it
discloses.

Pages 1-2 will need to be correspondingly amended in due
course and a reference to the citation to be inserted.

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2/3

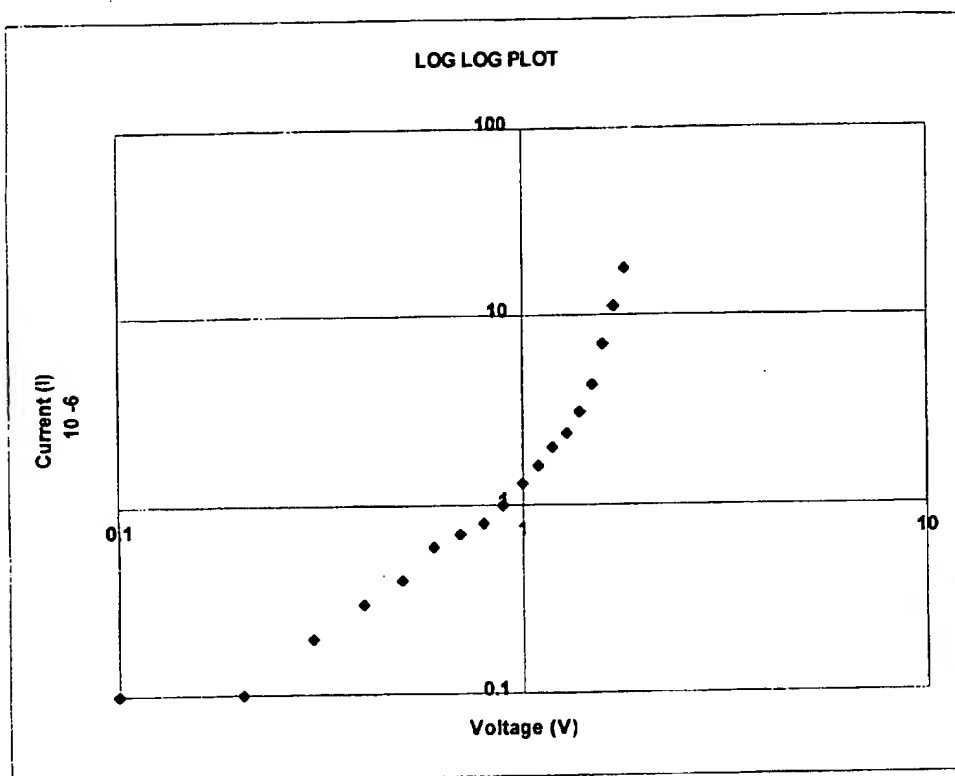
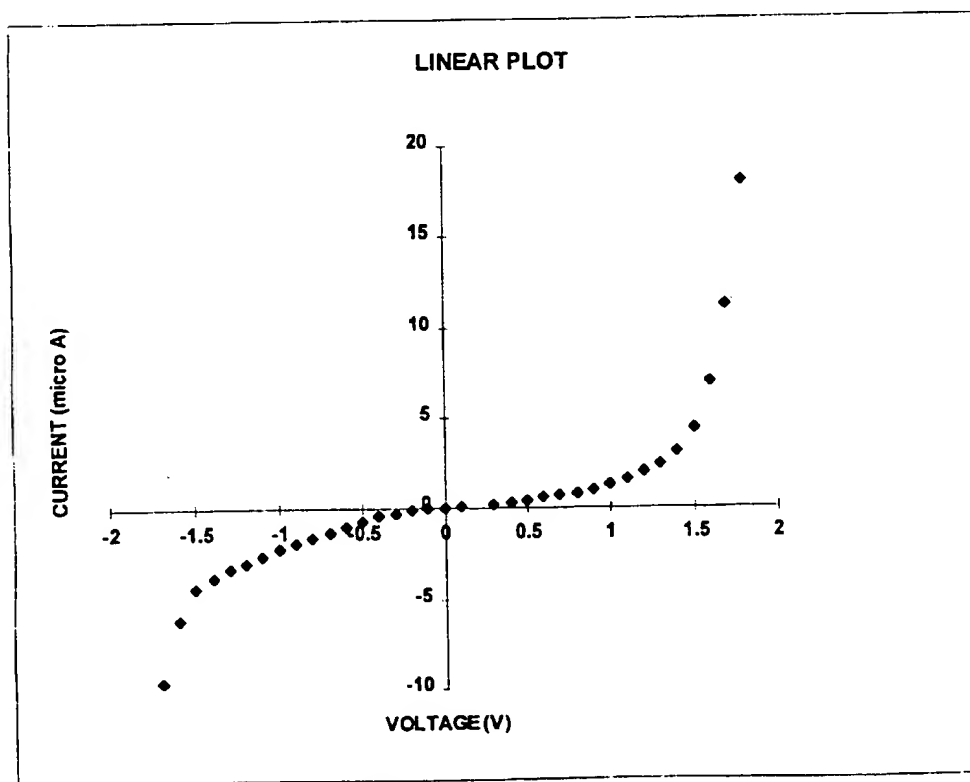


Figure 1



Figur 2

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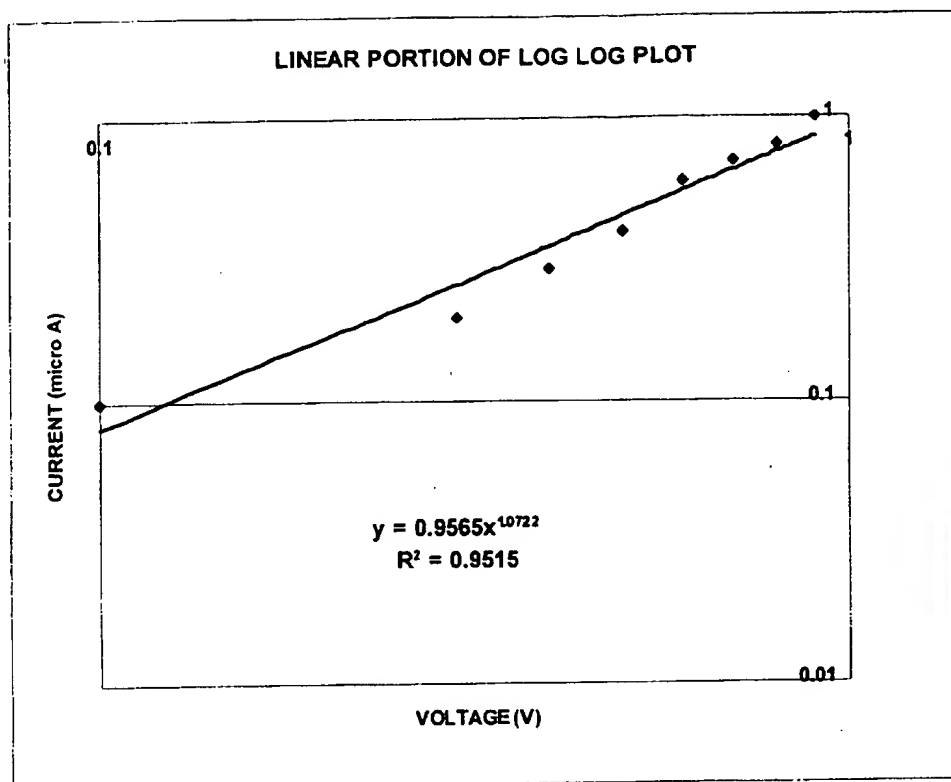


Figure 3

INTERNATIONAL SEARCH REPORT

International Application No

PC B 96/02954

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 H01B1/12 C08G61/12 C08G61/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 H01B C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 00882 A (TNO) 5 January 1995 see the whole document	1-5,10, 15,18
A	US 5 254 627 A (G.ROSSI & AL) 19 October 1993 see the whole document	1,3,8-10
A	PATENT ABSTRACTS OF JAPAN vol. 016, no. 200 (E-1201), 13 May 1992 & JP 04 032104 A (FUJI PHOTO FILM CO LTD), 4 February 1992, see abstract	1,2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

28 February 1997

Date of mailing of the international search report

12.03.97

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Authorized officer

Drouot, M-C

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. Application No
PCT/GB 96/02954

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9500882 A	05-01-95	NL 9301085 A	16-01-95
		AU 6985194 A	17-01-95
US 5254627 A	19-10-93	NONE	